

## STATEMENT

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and English and that I believe the following is true and correct  
translation of Japanese Patent Application No. 2002-017333.

Date: November 6, 2006

  
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Naoshi KITAMURA

PATENT OFFICE  
JAPANESE GOVERNMENT

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Applicant: FUJI PHOTO FILM CO., LTD.

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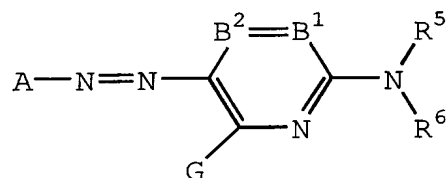
[Designation of Document]                      Specification

[Title of the Invention]    INK FOR INK JET RECORDING

[Claims]

[Claim 1]                      An ink for ink jet recording, comprising at least one dye dissolved or dispersed in the aqueous medium, the at least one dye being represented by the following formula (1), wherein the ink has a static surface tension of from 25 to 50 mN/m at 25°C:

Formula (1):



wherein A represents a 5-membered heterocyclic group;

B<sup>1</sup> and B<sup>2</sup> each represents =CR<sup>1</sup>- or -CR<sup>2</sup>= or either one of B<sup>1</sup> and B<sup>2</sup> represents a nitrogen atom and other represents =CR<sup>1</sup>- or -CR<sup>2</sup>=;

R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted;

G, R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a heterocyclic oxy carbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxy carbonyloxy group, an aryloxy carbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted; and

R<sup>1</sup> and R<sup>5</sup>, or R<sup>5</sup> and R<sup>6</sup> may combine to form a 5- or 6-membered ring.

[Claim 2]                      The ink for ink jet recording according to claim 1, which has a dynamic

surface tension of from 25 to 50 mN/m at 25°C.

[Claim 3] A method for inkjet recording using the ink for inkjet recording according to claim 1 or 2.

[Claim 4] A method for inkjet recording, comprising steps of: ejecting an ink droplet in accordance with a recording signal on an image-receiving material, the image-receiving material comprising an image-receiving layer that contains a white inorganic pigment particle on a support; and recording an image on the image-receiving material, wherein the ink droplet is the ink for inkjet recording according to claim 1 or 2.

[Detailed Description of the Invention]

[Technical Field to which the Invention Belongs]

The present invention relates to an ink for ink jet recording which can provide a recorded image having a high image quality, exhibit an excellent ink ejection stability and provide a recorded image having an excellent preservability.

[Background Art]

In recent years, with the spread of computers, ink jet printers have been widely used to print on paper, film, cloth, etc. at offices as well as at home.

Examples of ink jet recording method include a method which allows a piezoelectric element to give pressure that causes a droplet to be ejected, a method which comprises heating the ink to generate bubbles, causing a droplet to be ejected, a method involving the use of ultrasonic wave, and a method which uses electrostatic force to suck and discharge a droplet. As inks for these ink jet recording methods there are used aqueous inks, oil-based inks and solid (melt type) inks. Among these inks, aqueous inks are mainly used currently because they are relatively better than oil-based inks and solid (melt type) inks from the standpoint of possibility of attaining producibility, handleability, odor, safety, etc.

The dyes to be incorporated in these inks for ink jet recording are required to exhibit a high solubility in solvents (ink medium), allow a high density recording and have a good hue and an excellent fastness to light, heat, air, water and chemical, a good fixability to image-receiving materials, difficulty in running, an excellent preservability as an ink, no toxicity and a high purity and be available at a low cost. However, it is extremely difficult to seek coloring agents meeting these requirements to a high extent. In particular, excellent hue and fastness are contrary to each other in most cases, making it difficult to obtain coloring materials for magenta ink that can satisfy the aforesaid requirements and particularly difficult to find out dyestuffs which exhibit a good magenta hue and a light fastness high enough to withstand an oxidizing atmosphere at the same time.

Accordingly, although various dyes or dyestuffs for ink jet have been already proposed and practically used, it is the present situation that no dyestuffs that satisfying all the aforesaid requirements have been found yet. Known dyes and pigments provided with color index (C.I.) number can difficultly satisfy both the hue and fastness requirements for inks for ink jet recording.

As a dye which can enhance fastness there has been proposed an azo dye derived from an aromatic amine and a 5-membered heterocyclic amine described in JP-A-55-161856. However, these dyes have an undesirable hue in the yellow and cyan ranges and thus are disadvantageous in that they deteriorate color reproducibility. JP-A-61-36362 and JP-A-2-212566 disclose inks for ink jet recording for the purpose of accomplishing both hue and light fastness. However, the dyestuffs used in these publications have an insufficient water solubility when used as water-soluble ink. Further, the dyestuffs described in these publications are disadvantageous also in wet heat fastness when used as water-soluble ink for ink jet. As means for solving these problems there have been proposed an improved magenta dyestuff and an ink composition using the same described in JP-T-11-504958. Further, an ink for ink jet recording which comprises a pyrazolylaniline azo dyestuff to improve hue and light fastness is also described (Japanese Patent Application No. 2000-80733). However, these inks for ink jet recording leave something to be desired both in color reproducibility and fastness of output image.

Further, it was made obvious that there are some cases where an image recorded on a gloss paper of photographic image quality dedicated to ink jet exhibits a remarkably poor image preservability when put on the wall of a indoor room. The present inventors presume that this phenomenon is attributed to some oxidizing gases such as ozone in the air. Further, the blockade of air flow such as by enclosure in a glass frame makes it difficult for this phenomenon to occur, but this limits the working conditions.

This phenomenon is remarkable particularly with gloss paper of photographic image quality dedicated to ink jet and thus raises a great problem with the current ink jet recording process, which is required to provide a desired photographic quality image as one of important features.

#### [Problems that the Invention is to Solve]

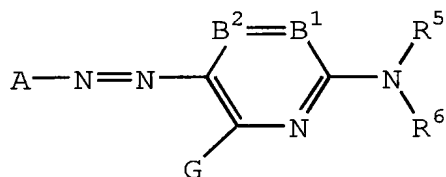
An aim of the present invention is to solve the problems with ink for ink jet recording which exhibits a high stability in ejection, is provided with a hue, is excellent in weathering resistance and causes no defects in water resistance and image quality.

[Means for Solving the Problems]

The objects of the present invention can be attained by the techniques described in the following 1 to 7.

1. An ink for ink jet recording, comprising at least one dye dissolved or dispersed in the aqueous medium, the at least one dye being represented by the following formula (1), wherein the ink has a static surface tension of from 25 to 50 mN/m at 25°C:

Formula (1):



wherein A represents a 5-membered heterocyclic group;

B<sup>1</sup> and B<sup>2</sup> each represents =CR<sup>1</sup>- or -CR<sup>2</sup>= or either one of B<sup>1</sup> and B<sup>2</sup> represents a nitrogen atom and other represents =CR<sup>1</sup>- or -CR<sup>2</sup>=;

R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted;

G, R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a heterocyclic oxy carbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxy carbonyloxy group, an aryloxy carbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted; and

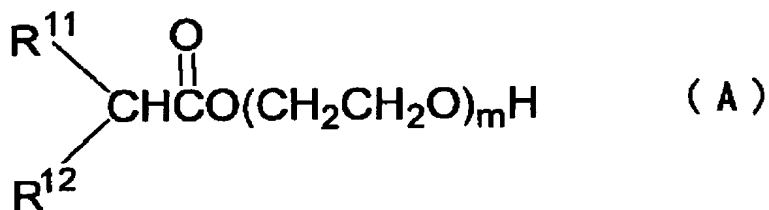
R<sup>1</sup> and R<sup>5</sup>, or R<sup>5</sup> and R<sup>6</sup> may combine to form a 5- or 6-membered ring.

2. The ink for ink jet recording according to item 1, which has a dynamic surface



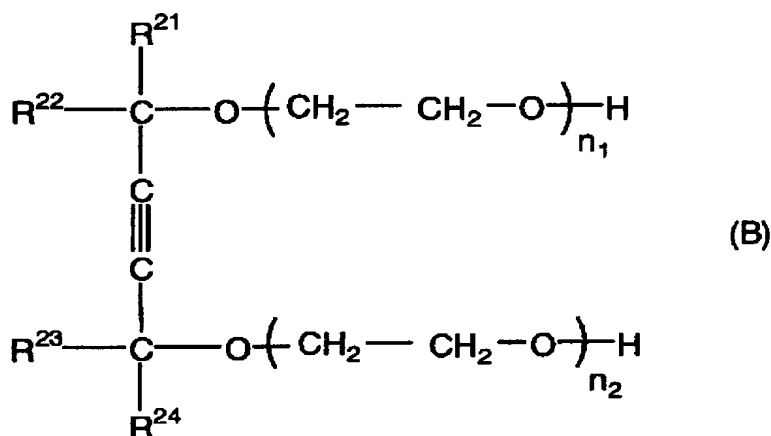
tension of from 25 to 50 mN/m at 25°C.

3. The ink for ink jet recording according to item 1 or 2, which comprises a compound represented by the following formula (A):



wherein  $\text{R}^{11}$  and  $\text{R}^{12}$  each represents a  $\text{C}_2$ - $\text{C}_{20}$  saturated hydrocarbon, and  $m$  represents from 2 to 40.

4. The ink for ink jet recording according to item 1 or 2, which comprises a compound represented by the following formula (B):



wherein  $\text{R}^{21}$ ,  $\text{R}^{22}$ ,  $\text{R}^{23}$  and  $\text{R}^{24}$  each independently represents a  $\text{C}_1$ - $\text{C}_6$ , and  $n_1$  and  $n_2$  each represents a number such that the sum of  $n_1$  and  $n_2$  is from 0 to 40

5. The ink for ink jet recording according to any one of items 1 to 3, which comprises an organic solvent having a boiling point of 150°C or more.

6. A method for inkjet recording using the ink for inkjet recording according to any one of items 1 to 5.

7. A method for inkjet recording, comprising steps of: ejecting an ink droplet in accordance with a recording signal on an image-receiving material, the image-receiving material comprising an image-receiving layer that contains a white inorganic pigment particle on a support; and recording an image on the image-receiving material, wherein the ink

droplet is the ink for inkjet recording according to any one of items 1 to 5.

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

The dye used in the inkjet recording ink of the invention is an azo dye containing an aromatic nitrogen-containing 6-membered heterocyclic ring as a coupling component and is represented by the formula (1).

In the formula (1), A represents a 5-membered heterocyclic group;

B<sup>1</sup> and B<sup>2</sup> each represents =CR<sup>1</sup>- or -CR<sup>2</sup>= or either one of B<sup>1</sup> and B<sup>2</sup> represents a nitrogen atom and the other represents =CR<sup>1</sup>- or -CR<sup>2</sup>=;

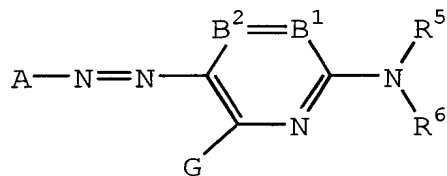
R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom or a substituent, the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted;

G, R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxy carbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxy carbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted; and

R<sup>1</sup> and R<sup>5</sup>, or R<sup>5</sup> and R<sup>6</sup> may combine to form a 5- or 6-membered ring.

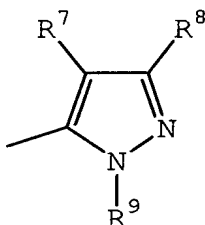
The dye of formula (1) is described in more detail.

Formula (1):



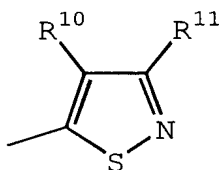
In formula (1), A represents a 5-membered heterocyclic group. Examples of the heteroatom of the heterocyclic ring include N, O and S. A is preferably a nitrogen-containing 5-membered heterocyclic ring and the heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or another heterocyclic ring. Preferred examples of the heterocyclic ring represented by A include a pyrazole ring, an imidazole ring, a thiazole ring, an isothiazole ring, a thiadiazole ring, a benzothiazole ring, a benzoxazole ring and a benzisothiazole ring. Each heterocyclic group may further have a substituent. Among these rings, more preferred are a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring and a benzothiazole ring represented by the following formulae (a) to (f):

Formula (a)

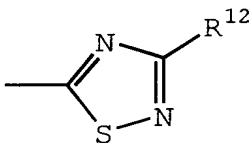


(c)

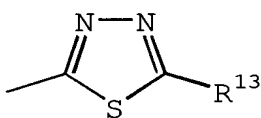
(b)



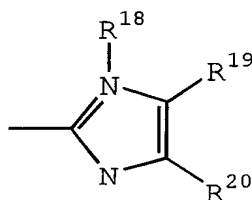
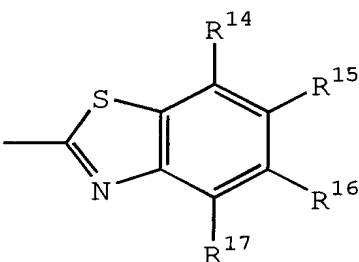
(d)



(e)



(f)



wherein  $R^7$  to  $R^{20}$  each represents the same substituent as G,  $R^1$  and  $R^2$  in formula (1).

Among formulae (a) to (f), preferred are a pyrazole ring and an isothiazole ring represented by formulae (a) and (b), and most preferred is a pyrazole ring represented by formula (a).

In formula (1),  $B^1$  and  $B^2$  each represents  $=CR^1-$  or  $-CR^2=$  or either one of  $B^1$  and  $B^2$  represents a nitrogen atom and the other represents  $=CR^1-$  or  $-CR^2=$ .  $B^1$  and  $B^2$  each preferably represents  $=CR^1-$  or  $-CR^2=$ .

$R^5$  and  $R^6$  each independently represents a hydrogen atom or a substituent, the

substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and the hydrogen atom of each substituent may be substituted.

R<sup>5</sup> and R<sup>6</sup> each is preferably a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group, and the hydrogen atom of each substituent may be substituted, but R<sup>5</sup> and R<sup>6</sup> are not a hydrogen atom at the same time.

G, R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a substituent, the substituent is a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxy carbonyloxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxy carbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and the hydrogen atom of each substituent may be substituted.

G is preferably a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, a heterocyclic oxy group, an amino group, an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxy carbonylamino group, an alkylthio group, an arylthio group or a heterocyclic thio group, more preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group (preferably an anilino group) or an acylamino group, and the hydrogen atom of each substituent may be substituted.

R<sup>1</sup> and R<sup>2</sup> each is preferably a hydrogen atom, an alkyl group, a halogen atom, an alkoxycarbonyl group, a carboxyl group, a carbamoyl group, a hydroxy group, an alkoxy

group or a cyano group, and the hydrogen atom of each substituent may be substituted.

$R^1$  and  $R^5$ , or  $R^5$  and  $R^6$  may combine to form a 5- or 6-membered ring.

When A has a substituent or when the substituent  $R^1$ ,  $R^2$ ,  $R^5$ ,  $R^6$  or G further has a substituent, examples of the substituent include the substituents described above for G,  $R^1$  and  $R^2$ .

In the case where the dye of the present invention is a water-soluble dye, the dye preferably has further an ionic hydrophilic group as a substituent on any position of A,  $R^1$ ,  $R^2$ ,  $R^5$ ,  $R^6$  and G. Examples of the ionic hydrophilic group as a substituent include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium).

The terms (substituents) used in the present invention are described below. These terms each is common among different symbols in formula (1) and also in formula (1a) shown later.

The halogen atom includes a fluorine atom, a chlorine atom and a bromine atom.

The aliphatic group means an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an aralkyl group and a substituted aralkyl group. The "substituted" used for a "substituted alkyl group" and the like in the present invention means that the hydrogen atom present in an "alkyl group" or the like is substituted, for example, by a substituent described above for G,  $R^1$  and  $R^2$ .

The aliphatic group may be branched or may form a ring. The number of carbon atoms in the aliphatic group is preferably from 1 to 20, more preferably from 1 to 16. The aryl moiety in the aralkyl group and the substituted aralkyl group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. Examples of the aliphatic group include a methyl group, an ethyl group, a butyl group, an isopropyl group, a tert-butyl group, a hydroxyethyl group, a methoxyethyl group, a cyanoethyl group, a trifluoromethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a cyclohexyl group, a benzyl group, a 2-phenethyl group, a vinyl group and an allyl group.

The aromatic group means an aryl group and a substituted aryl group. The aryl

group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. The number of carbon atoms in the aromatic group is preferably from 6 to 20, more preferably from 6 to 16.

Examples of the aromatic group include a phenyl group, a p-tolyl group, a p-methoxyphenyl group, an o-chlorophenyl group and an m-(3-sulfopropylamino)phenyl group.

The heterocyclic group includes a substituted heterocyclic group. In the heterocyclic group, the heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or another heterocyclic ring. The heterocyclic group is preferably a 5- or 6-membered heterocyclic group. Examples of the substituent of the substituted heterocyclic group include an aliphatic group, a halogen atom, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfamoyl group, a carbamoyl group and an ionic hydrophilic group. Examples of the heterocyclic group include a 2-pyridyl group, a 2-thienyl group, a 2-thiazolyl group, a 2-benzothiazolyl group, a 2-benzoxazolyl group and a 2-furyl group.

The carbamoyl group includes a substituted carbamoyl group. Examples of the substituent therefor include an alkyl group. Examples of the carbamoyl group include a methylcarbamoyl group and a dimethylcarbamoyl group.

The alkoxycarbonyl group includes a substituted alkoxycarbonyl group. The alkoxycarbonyl group is preferably an alkoxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted alkoxycarbonyl group include an ionic hydrophilic group. Examples of the alkoxycarbonyl group include a methoxycarbonyl group and an ethoxycarbonyl group.

The aryloxycarbonyl group includes a substituted aryloxycarbonyl group. The aryloxycarbonyl group is preferably an aryloxycarbonyl group having from 7 to 20 carbon atoms. Examples of the substituent of the substituted aryloxycarbonyl group include an ionic hydrophilic group. Examples of the aryloxycarbonyl group include a phenoxy carbonyl group.

The heterocyclic oxycarbonyl group includes a substituted heterocyclic oxycarbonyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic oxycarbonyl group is preferably a heterocyclic oxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic oxycarbonyl group include an ionic hydrophilic group. Examples of the heterocyclic oxycarbonyl group include a 2-pyridyloxycarbonyl group.

The acyl group includes a substituted acyl group. The acyl group is preferably an acyl group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted acyl group include an ionic hydrophilic group. Examples of the acyl group include an acetyl group and a benzoyl group.

The alkoxy group includes a substituted alkoxy group. The alkoxy group is preferably an alkoxy group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted alkoxy group include an alkoxy group, a hydroxyl group and an ionic hydrophilic group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an isopropoxy group, a methoxyethoxy group, a hydroxyethoxy group and a 3-carboxypropoxy group.

The aryloxy group includes a substituted aryloxy group. The aryloxy group is preferably an aryloxy group having from 6 to 20 carbon atoms. Examples of the substituent of the substituted aryloxy group include an alkoxy group and an ionic hydrophilic group. Examples of the aryloxy group include a phenoxy group, a p-methoxyphenoxy group and an o-methoxyphenoxy group.

The heterocyclic oxy group includes a substituted heterocyclic oxy group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic oxy group is preferably a heterocyclic oxy group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic oxy group include an alkyl group, an alkoxy group and an ionic hydrophilic group. Examples of the heterocyclic oxy group include a 3-pyridyloxy group and a 3-thienyloxy group.

The silyloxy group is preferably a silyloxy group substituted by an aliphatic or aromatic group having from 1 to 20 carbon atoms. Examples of the silyloxy group include a trimethylsilyloxy group and a diphenylmethylsilyloxy group.

The acyloxy group includes a substituted acyloxy group. The acyloxy group is preferably an acyloxy group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted acyloxy group include an ionic hydrophilic group. Examples of the acyloxy group include an acetoxy group and a benzoyloxy group.

The carbamoyloxy group includes a substituted carbamoyloxy group. Examples of the substituent therefor include an alkyl group. Examples of the carbamoyloxy group include an N-methylcarbamoyloxy group.

The alkoxycarbonyloxy group includes a substituted alkoxycarbonyloxy group. The alkoxycarbonyloxy group is preferably an alkoxycarbonyloxy group having from 2 to 20 carbon atoms. Examples of the alkoxycarbonyloxy group include a methoxycarbonyloxy

group and an isopropoxycarbonyloxy group.

The aryloxycarbonyloxy group includes a substituted aryloxycarbonyloxy group. The aryloxycarbonyloxy group is preferably an aryloxycarbonyloxy group having from 7 to 20 carbon atoms. Examples of the aryloxycarbonyloxy group include a phenoxycarbonyloxy group.

The amino group includes a substituted amino group. Examples of the substituent therefor include an alkyl group, an aryl group and a heterocyclic group, and the alkyl group, the aryl group and the heterocyclic group each may further have a substituent. The alkylamino group includes a substituted alkylamino group. The alkylamino group is preferably an alkylamino group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted alkylamino group include an ionic hydrophilic group. Examples of the alkylamino group include a methylamino group and a diethylamino group.

The arylamino group includes a substituted arylamino group. The arylamino group is preferably an arylamino group having from 6 to 20 carbon atoms. Examples of the substituent of the substituted arylamino group include a halogen atom and an ionic hydrophilic group. Examples of the arylamino group include a phenylamino group and a 2-chlorophenylamino group.

The heterocyclic amino group includes a substituted heterocyclic amino group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic amino group is preferably a heterocyclic amino group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic amino group include an alkyl group, a halogen atom and an ionic hydrophilic group.

The acylamino group includes a substituted acylamino group. The acylamino group is preferably an acylamino group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted acylamino group include an ionic hydrophilic group. Examples of the acylamino group include an acetylamino group, a propionylamino group, a benzoylamino group, an N-phenylacetylamino group and a 3,5-disulfobenzoylamino group.

The ureido group includes a substituted ureido group. The ureido group is preferably a ureido group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted ureido group include an alkyl group and an aryl group. Examples of the ureido group include a 3-methylureido group, a 3,3-dimethylureido group and a 3-phenylureido group.

The sulfamoylamino group includes a substituted sulfamoylamino group.



Examples of the substituent therefor include an alkyl group. Examples of the sulfamoylamino group include an N,N-dipropylsulfamoylamino group.

The alkoxycarbonylamino group includes a substituted alkoxycarbonylamino group. The alkoxycarbonylamino group is preferably an alkoxycarbonylamino group having from 2 to 20 carbon atoms. Examples of the substituent of the substituted alkoxycarbonylamino group include an ionic hydrophilic group. Examples of the alkoxycarbonylamino group include an ethoxycarbonylamino group.

The aryloxy carbonylamino group includes a substituted aryloxy carbonylamino group. The aryloxy carbonylamino group is preferably an aryloxy carbonylamino group having from 7 to 20 carbon atoms. Examples of the substituent of the substituted aryloxy carbonylamino group include an ionic hydrophilic group. Examples of the aryloxy carbonylamino group include a phenoxycarbonylamino group.

The alkylsulfonylamino group and the arylsulfonylamino group include a substituted alkylsulfonylamino group and a substituted arylsulfonylamino group, respectively. The alkylsulfonylamino group and the arylsulfonylamino group are preferably an alkylsulfonylamino group having from 1 to 20 carbon atoms and an arylsulfonylamino group having from 7 to 20 carbon atoms, respectively. Examples of the substituent of the substituted alkylsulfonylamino group and substituted arylsulfonylamino group include an ionic hydrophilic group. Examples of the alkylsulfonylamino group and arylsulfonylamino group include a methylsulfonylamino group, an N-phenyl-methylsulfonylamino group, a phenylsulfonylamino group and a 3-carboxyphenylsulfonylamino group.

The heterocyclic sulfonylamino group includes a substituted heterocyclic sulfonylamino group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfonylamino group is preferably a heterocyclic sulfonylamino group having from 1 to 12 carbon atoms. Examples of the substituent of the substituted heterocyclic sulfonylamino group include an ionic hydrophilic group. Examples of the heterocyclic sulfonylamino group include a 2-thienylsulfonylamino group and a 3-pyridylsulfonylamino group.

The alkylthio group, the arylthio group and the heterocyclic thio group include a substituted alkylthio group, a substituted arylthio group and a substituted heterocyclic thio group, respectively. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The alkylthio group, the arylthio group and the heterocyclic thio group are preferably an alkylthio group having from 1 to 20 carbon atoms, an arylthio group having from 1 to 20 carbon atoms and a heterocyclic thio group having

from 1 to 20 carbon atoms, respectively. Examples of the substituent of the substituted alkylthio group, substituted arylthio group and substituted heterocyclic thio group include an ionic hydrophilic group. Examples of the alkylthio group, arylthio group and heterocyclic thio group include a methylthio group, a phenylthio group and a 2-pyridylthio group.

The alkylsulfonyl group and the arylsulfonyl group include a substituted alkylsulfonyl group and a substituted arylsulfonyl group, respectively. Examples of the alkylsulfonyl group and arylsulfonyl group include a methylsulfonyl group and a phenylsulfonyl group.

The heterocyclic sulfonyl group includes a substituted heterocyclic sulfonyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfonyl group is preferably a heterocyclic sulfonyl group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic sulfonyl group include an ionic hydrophilic group. Examples of the heterocyclic sulfonyl group include a 2-thienylsulfonyl group and a 3-pyridylsulfonyl group.

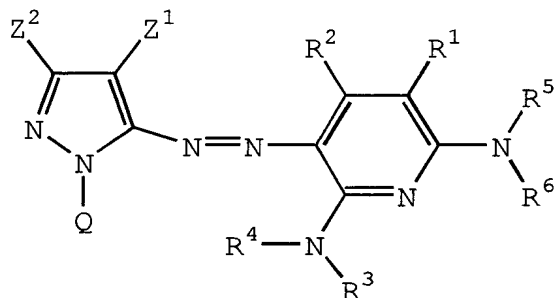
The alkylsulfinyl group and the arylsulfinyl group include a substituted alkylsulfinyl group and a substituted arylsulfinyl group, respectively. Examples of the alkylsulfinyl group and arylsulfinyl group include a methylsulfinyl group and a phenylsulfinyl group.

The heterocyclic sulfinyl group includes a substituted heterocyclic sulfinyl group. Examples of the heterocyclic ring include the heterocyclic rings described above for the heterocyclic group. The heterocyclic sulfinyl group is preferably a heterocyclic sulfinyl group having from 1 to 20 carbon atoms. Examples of the substituent of the substituted heterocyclic sulfinyl group include an ionic hydrophilic group. Examples of the heterocyclic sulfinyl group include a 4-pyridylsulfinyl group.

The sulfamoyl group includes a substituted sulfamoyl group. Examples of the substituent therefor include an alkyl group. Examples of the sulfamoyl group include a dimethylsulfamoyl group and a di-(2-hydroxyethyl)sulfamoyl group.

Among the dyes represented by formula (1), particularly preferred is a structure represented by the following formula (1a):

Formula (1a):



In formula (1a), R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup> and R<sup>6</sup> have the same meanings as in formula (1).

R<sup>3</sup> and R<sup>4</sup> each independently represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group. R<sup>3</sup> and R<sup>4</sup> each is preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group or a heterocyclic group.

Z<sup>1</sup> represents an electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.20 or more. Z<sup>1</sup> is preferably an electron-withdrawing group having a  $\sigma_p$  value of 0.30 or more, more preferably 0.45 or more, still more preferably 0.60 to more, but the  $\sigma_p$  value preferably does not exceed 1.0. Specific preferred examples of this substituent include electron-withdrawing substituents described later. Among those, preferred are an acyl group having from 2 to 20 carbon atoms, an alkylloxycarbonyl group having from 2 to 20 carbon atoms, a nitro group, a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, an arylsulfonyl group having from 6 to 20 carbon atoms, a carbamoyl group having from 1 to 20 carbon atoms and a halogenated alkyl group having from 1 to 20 carbon atoms, more preferred are a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms and an arylsulfonyl group having from 6 to 20 carbon atoms, and most preferred is a cyano group.

Z<sup>2</sup> represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group or a heterocyclic group. Z<sup>2</sup> is preferably an aliphatic group, more preferably an alkyl group having from 1 to 6 carbon atoms.

Q represents a hydrogen atom or a substituent and the substituent is an aliphatic group, an aromatic group or a heterocyclic group. Q is preferably a group comprising a nonmetallic atom group necessary for forming a 5-, 6-, 7- or 8-membered ring. The 5-, 6-, 7- or 8-membered ring may be substituted, may be a saturated ring or may have an unsaturated bond. Q is more preferably an aromatic group or a heterocyclic group.

Preferred examples of the nonmetallic atom include a nitrogen atom, an oxygen atom, a sulfur atom and a carbon atom. Specific examples of the ring structure include a benzene ring, a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, a cyclooctane ring, a cyclohexene ring, a pyridine ring, a pyrimidine ring, a pyrazine ring, a pyridazine ring, a triazine ring, an imidazole ring, a benzimidazole ring, an oxazole ring, a benzoxazole ring, a thiazole ring, a benzothiazole ring, an oxane ring, a sulfolane ring and a thiane ring.

The hydrogen atom of each substituent described in regard to formula (1a) may be substituted. Examples of the substituent include the substituents described in regard to formula (1), the groups described as examples for G, R<sup>1</sup> and R<sup>2</sup>, and ionic hydrophilic groups.

Here, the Hammett's substituent constant  $\sigma_p$  value used in the present invention is described. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a  $\sigma_p$  value and a  $\sigma_m$  value and these values can be found in a large number of general publications but these are described in detail, for example, in J.A. Dean (compiler), *Lange's Handbook of Chemistry*, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979). In the present invention, each substituent is limited or described by using the Hammett's substituent constant  $\sigma_p$  but this does not mean that the substituent is limited only to those having a known value which can be found in the above-described publications. Needless to say, the substituent includes substituents of which  $\sigma_p$  value is not known in publications but when measured based on the Hammett's rule, falls within the range specified. Furthermore, although formula (1a) of the present invention include those which are not a benzene derivative, the  $\sigma_p$  value is used as a measure for showing the electron effect of the substituent irrespective of the substitution site. In the present invention, the  $\sigma_p$  value is used in such a meaning.

Examples of the electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.60 or more include a cyano group, a nitro group, an alkylsulfonyl group (e.g., methylsulfonyl) and an arylsulfonyl group (e.g., phenylsulfonyl).

Examples of the electron-withdrawing group having a Hammett's  $\sigma_p$  value of 0.45 or more include, in addition to those described above, an acyl group (e.g., acetyl), an alkoxycarbonyl group (e.g., dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., m-chlorophenoxycarbonyl), an alkylsulfinyl group (e.g., n-propylsulfinyl), an arylsulfinyl

group (e.g., phenylsulfinyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl) and a halogenated alkyl group (e.g., trifluoromethyl).

Examples of the electron-withdrawing group having a Hammett's substituent constant  $\sigma_p$  value of 0.30 or more include, in addition to those described above, an acyloxy group (e.g., acetoxy), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a halogenated alkoxy group (e.g., trifluoromethyloxy), a halogenated aryloxy group (e.g., pentafluorophenyloxy), a sulfonyloxy group (e.g., methylsulfonyloxy), a halogenated alkylthio group (e.g., difluoromethylthio), an aryl group substituted by two or more electron-withdrawing groups having a  $\sigma_p$  value of 0.15 or more (e.g., 2,4-dinitrophenyl, pentachlorophenyl) and a heterocyclic ring (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl).

Specific examples of the electron-withdrawing group having a  $\sigma_p$  value of 0.20 or more include, in addition to those described above, a halogen atom.

The preferred combination of substituents in the azo dye represented by formula (1) is described below.  $R^5$  and  $R^6$  each is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a sulfonyl group or an acyl group, more preferably a hydrogen atom, an aryl group, a heterocyclic group or a sulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group. However,  $R^5$  and  $R^6$  are not a hydrogen atom at the same time.

G is preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an amino group or an acylamino group, more preferably a hydrogen atom, a halogen atom, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group or an acylamino group.

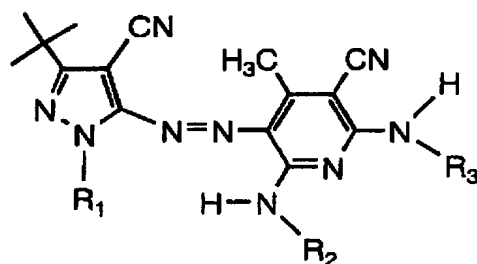
A is preferably a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring or a benzothiazole ring, more preferably a pyrazole ring or an isothiazole ring, and most preferably a pyrazole ring.

$B^1$  and  $B^2$  each is preferably  $=CR^1-$  or  $-CR^2=$ , and  $R^1$  and  $R^2$  each is preferably a hydrogen atom, an alkyl group, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, a hydroxyl group, an alkoxy group or an alkoxycarbonyl group, more preferably a hydrogen atom, an alkyl group, a carboxyl group, a cyano group or a carbamoyl group.

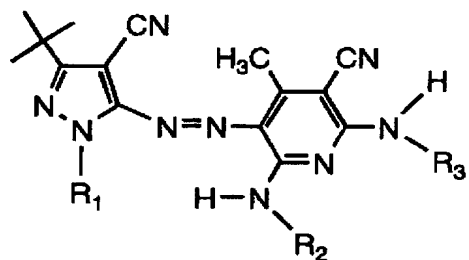
As for the preferred combination of substituents in the compound represented by formula (1), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups

is more preferred, and a compound where all substituents are the preferred groups is most preferred.

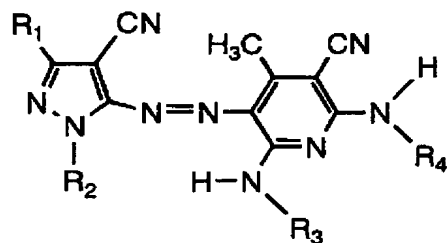
Specific examples of the azo dye represented by formula (1) are shown below, but the azo dye for use in the present invention is not limited to those shown below.



Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
a-1			
a-2			
a-3			
a-4			
a-5			

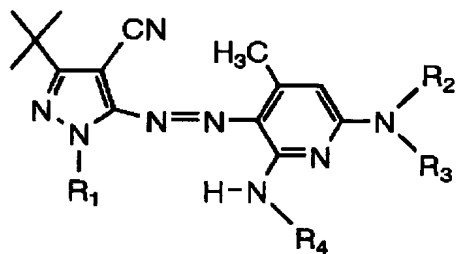


Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
a-6			
a-7			
a-8			
a-9			
a-10			

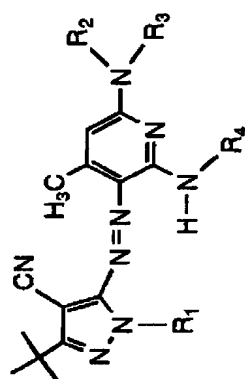



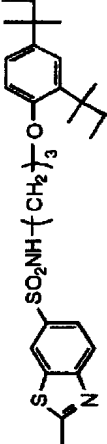
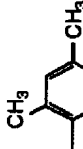
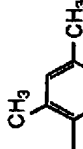

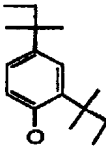
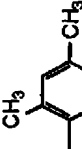
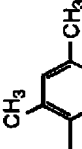
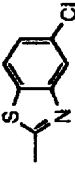
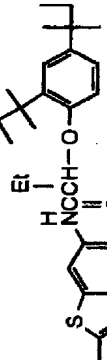
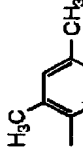
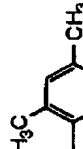

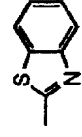
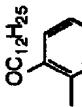
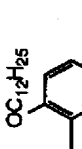
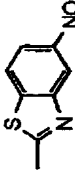
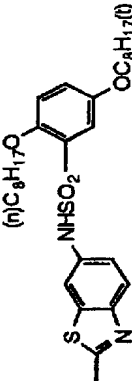
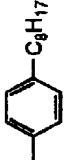
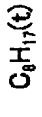
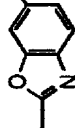

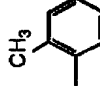
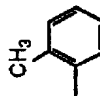
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-11				
a-12				
a-13				
a-14				
a-15				
a-16				
a-17				

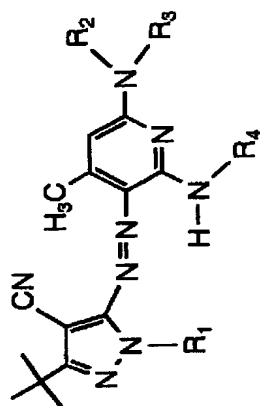




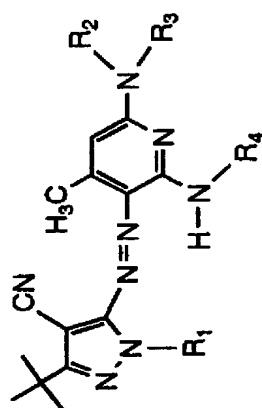
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-18				
a-19		-SO <sub>2</sub> CH <sub>3</sub>		
a-20		-COCH <sub>3</sub>	C <sub>8</sub> H <sub>17</sub> (t)	C <sub>8</sub> H <sub>17</sub> (t)
a-21		-SO <sub>2</sub> CH <sub>3</sub>		C <sub>8</sub> H <sub>17</sub> (t)
a-22		H		
a-23		H		
a-24		H		
a-25				



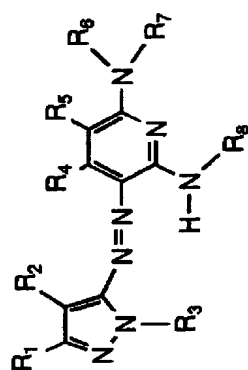
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-26				
a-27				
a-28				
a-29				
a-30				
a-31				



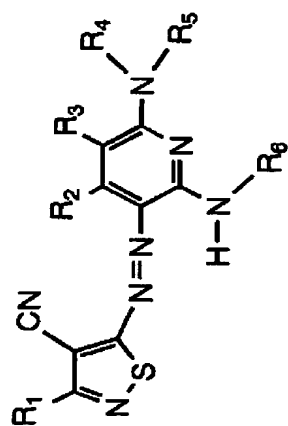
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-32				
a-33				
a-34				
a-35				



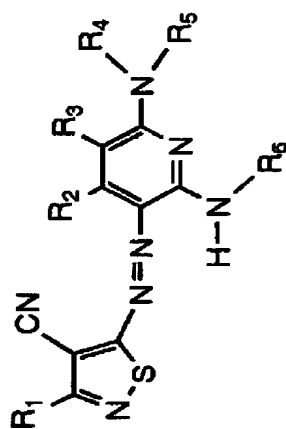
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
a-36				
a-37				
a-38				
a-39				
a-40				



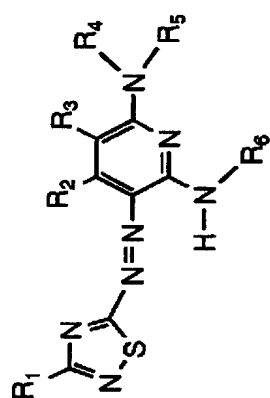
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>
a-41		CN		H	CONH <sub>2</sub>	SO <sub>2</sub> CH <sub>3</sub>		
a-42		Br		COOEt	H		C <sub>8</sub> H <sub>17</sub> (t)	COCH <sub>3</sub>
a-43		SO <sub>2</sub> CH <sub>3</sub>		CONH <sub>2</sub>	H			
a-44		CN		H	H			SO <sub>2</sub> CH <sub>3</sub>
a-45		Br		H	CONH <sub>2</sub>			
a-46		CN		CH <sub>3</sub>	H			



Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
b-1	CH <sub>3</sub>	CH <sub>3</sub>	CN	H		
b-2	CH <sub>3</sub>	CH <sub>3</sub>	CN	H		
b-3	CH <sub>3</sub>	CH <sub>3</sub>	CONH <sub>2</sub>	H		
b-4	CH <sub>3</sub>	CH <sub>3</sub>	H	H		
b-5	CH <sub>3</sub>	H	CN	H		

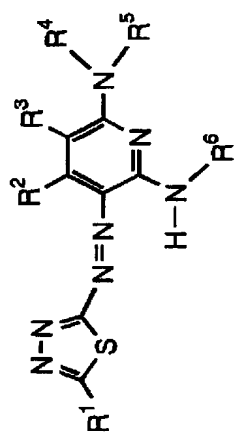


Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
b-6	CH <sub>3</sub>	CH <sub>3</sub>	H			
b-7	CH <sub>3</sub>	CH <sub>3</sub>	H			
b-8	CH <sub>3</sub>	H	H	SO <sub>2</sub> CH <sub>3</sub>	SO <sub>2</sub> Na	SO <sub>2</sub> Na

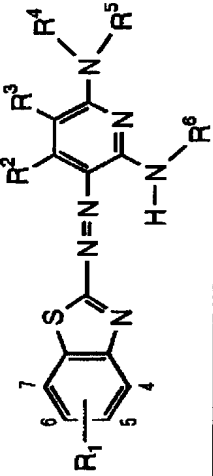
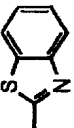
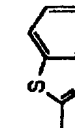
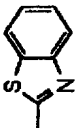
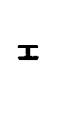
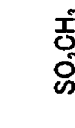


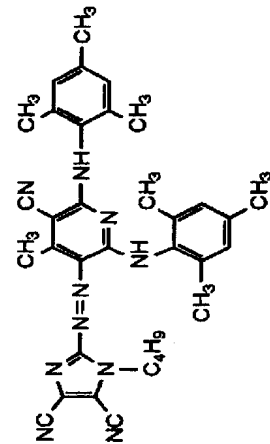
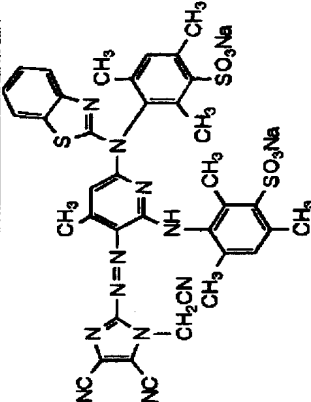


Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
c-1	-SCH <sub>3</sub>	CH <sub>3</sub>	CN	H	C <sub>8</sub> H <sub>17</sub> (t)	
c-2		H	CONH <sub>2</sub>	H		
c-3		CH <sub>3</sub>	H			
c-4	-CH <sub>3</sub>	CH <sub>3</sub>	H			
c-5		H	H			C <sub>8</sub> H <sub>17</sub> (t)





Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
d-1	Me	CH <sub>3</sub>	CN	H		
d-2	Me	CH <sub>3</sub>	CN	H		
d-3	Me	H	H			
d-4	Ph	CH <sub>3</sub>	CONH <sub>2</sub>	H		
d-5	Ph	CH <sub>3</sub>	H			

					
Dye	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub> R <sub>6</sub>
e-1	5-Cl	CH <sub>3</sub>	CONH <sub>2</sub>	H	C <sub>8</sub> H <sub>17</sub> (t) C <sub>8</sub> H <sub>17</sub> (t)
e-2	5,6-diCl	H	H		C <sub>8</sub> H <sub>17</sub> (t) 
e-3	5,6-diCl	CH <sub>3</sub>	H		COCH <sub>3</sub> COCH <sub>3</sub>
e-4	5-CH <sub>3</sub>	H	CN	H	 SO <sub>3</sub> K 
e-5	5-NO <sub>2</sub>	CH <sub>3</sub>	H	SO <sub>2</sub> CH <sub>3</sub>	 CH <sub>3</sub> 
f-1					
f-2					

The inkjet recording ink of the present invention (sometimes referred to as "the ink of the present invention") has at least one azo dye, as mentioned above, dissolved or dispersed in an aqueous medium, and the content of the azo dye is preferably from 0.2 to 20

mass%, more preferably from 0.5 to 15 mass%.

In the ink of the present invention, other dyes may be used in combination with the azo dye so as to obtain a full color image or adjust the color tone. Examples of the dye which can be used in combination include the followings.

As the examples of yellow dyes, aryl and heterylazo dyes having, as the coupling component, e.g., phenols, naphthols, anilines, pyrazolones, pyridones, or open chain type active methylene compounds; azomethine dyes having, as the coupling component, e.g., open chain type active methylene compounds; methine dyes, e.g., a benzylidene dye and a monomethine oxonol dye; and quinone dyes, e.g., a naphthoquinone dye and an anthraquinone dye, are exemplified. Besides these dyes, quinophthalone dyes, nitronitroso dyes, acridine dyes and acridinone dyes can be exemplified. These dyes may be dyes which develop yellow color after a part of the chromophore is dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal and ammonium, may be an organic cation such as pyridinium and a quaternary ammonium salt, or may be a polymer cation having these cations as the partial structure.

As the examples of magenta dyes, aryl and heterylazo dyes having, as the coupling component, e.g., phenols, naphthols or anilines; azomethine dyes having, as the coupling component, e.g., pyrazolones or pyrazolotriazoles; methine dyes, e.g., an arylidene dye, a styryl dye, a merocyanine dye, and an oxonol dye; carbonium dyes, e.g., a diphenylmethane dye, a triphenylmethane dye and a xanthene dye; quinone dyes, e.g., a naphthoquinone dye, an anthraquinone dye and an anthrapyridone dye; and condensed polycyclic dyes, e.g., a dioxazine dye, are exemplified. These dyes may be dyes which develop magenta color after a part of the chromophore is dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal and ammonium, may be an organic cation such as pyridinium and a quaternary ammonium salt, or may be a polymer cation having these cations as the partial structure.

As the examples of cyan dyes, azomethine dyes, e.g., an indoaniline dye and an indophenol dye; polymethine dyes, e.g., a cyanine dye, an oxonol dye and a merocyanine dye; carbonium dyes, e.g., a diphenylmethane dye, a triphenylmethane dye and a xanthene dye; phthalocyanine dyes; anthraquinone dyes; aryl and heterylazo dyes having, as the coupling component, e.g., phenols, naphthols or anilines; and indigo-thioindigo dyes are exemplified. These dyes may be dyes which develop cyan color after a part of the chromophore is dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal and ammonium, may be an organic cation such as pyridinium and a

quaternary ammonium salt, or may be a polymer cation having these cations as the partial structure.

A black dye such as a polyazo dye can also be used.

The dyes containing an azo dye to be used in the present invention is substantially water-soluble or water-dispersible. In some detail, the solubility or dispersibility of the dye in water at 20°C is 2% by weight or more, preferably 5% by weight or more.

The ink for ink jet recording to be used in the present invention has a static surface tension of from 25 to 50 mN/m at 25°C. Preferably, it is from 30 to 40 mN/m at 25°C. When the static surface tension of the ink exceeds 50 mN/m, the resulting ink exhibits a drastic deterioration in print quality such as ejection stability and resistance to bleeding and whisker during color mixing. On the contrary, when the static surface tension of the ink falls below 25 mN/m, the resulting ink can be attached to hard surface when ejected, causing defective printing.

As the static surface tension measuring methods there are known capillary rise method, dropping method, and ring method, but, in the invention, as the static surface tension measuring method there is used a perpendicular plate method.

When a thin glass or platinum plate is hanged vertically while a part thereof being dipped in a liquid, surface tension of the liquid acts downward along the length of the plate in contact with the liquid. The surface tension is measured by balancing this force by a upward force that hangs the plate.

The dynamic surface tension of the ink to be used in the present invention is preferably from 25 to 50 mN/m, more preferably from 30 to 40 mN/m at 25°C. As dynamic surface tension measuring methods there are known vibration jet method, meniscus dropping method and maximum bubble pressure method as disclosed in "Shinjikken Kagaku Koza (New Institute of Experimental Chemistry), Vol.18 ed., Kaimen to Koroido (Interface and Colloid)", Maruzen, pp. 69 – 90 (1977), and a liquid film destruction method is known as disclosed in JP-A-3-2064, but, in the present invention, as the dynamic surface tension measuring method there is used a differential bubble pressure method. The principle and method of effecting this measuring method will be described hereinafter.

When bubbles are formed in a solution to which a surfactant is added and which has been stirred to uniformity, a new gas-liquid interface is produced, and surface active agent molecules in the solution then gather on the surface of water at a constant rate. The bubble rate (rate of formation of bubbles) is changed. As the formation rate decreases, more surface active agent gather on the surface of bubbles, reducing the maximum bubble pressure

shortly before the burst of bubbles, and the maximum bubble pressure (surface tension) with respect to bubble rate can be thus detected. In the measurement of dynamic surface tension in the present invention, bubbles are formed in a solution using a large probe and a small probe, the differential pressure of the two probes in the state of maximum bubble pressure is measured, and the dynamic surface tension is then calculated from the differential pressure.

Using a surface tension adjustor, the surface tension of the ink of the present invention can be adjusted to the aforementioned range.

Examples of the surface tension adjustor employable herein include nonionic, cationic or anionic surface active agents. Examples of the anionic surface active agent include aliphatic acid salts, alkylsulfuric acid ester salts, alkylbenzenesulfonates (e.g., alkylbenzenesulfoante, petroleum sulfoante), dialkylsulfosuccinates, alkylphosphoric acid esters, naphthalenesulfonic acid-formalin condensates, and polyoxyethylenealkylsulfuric acid esters. Examples of the nonionic surface active agent include acetylene-based diols (e.g., 2,4,7,9-tetramethyl-5-decyne-4,7-diol), polyoxyethylenealkyl ethers (e.g., polyoxyethylenedecyl ether, ethylene oxide adduct of acetylene-based diol), polyoxyethylenealiphatic acid esters, sorbitanaliphatic acid esters, polyoxyethylenesorbitanaliphatic acid esters, polyoxyethylenealkylamines, glycerinaliphatic acid esters, and oxyethyleneoxypropylene block copolymers.

Further, amine oxide-based amphoteric surface active agents such as N,N-dimethyl-N-alkylamine oxide are preferred. Moreover, those listed as surface active agents in JP-A-59-157,636, pp. 37 – 38, and Research Disclosure No. 308119, 1989, may be used.

Anionic surface active agents having a two-chain or branched hydrophobic moiety, anionic or nonionic surface active agents having a hydrophilic group in the vicinity of the center of hydrophobic moiety and nonionic surface active agents having a two-chain or branched hydrophobic moiety are preferred because they can be difficultly precipitated or separated out from the ink and cause little foaming.

Examples of the nonionic surface active agents having a two-chain or branched hydrophobic moiety include a compound represented by the formula (A).

In the formula (A),  $R^{11}$  and  $R^{12}$  each represents a  $C_2$ - $C_{20}$  saturated hydrocarbon preferably,  $C_4$ - $C_{13}$  saturated hydrocarbon, and more preferably, the sum of the number of carbon atoms in  $R^{11}$  and  $R^{12}$  is from 8 to 18. The suffix m represents from 2 to 40, preferably from 4 to 30, more preferably from 4 to 20.

The compound represented by the formula (A) can be obtained by the method

described in Takehiko Fujimoto, "Shin Kaimen Kasseizai Nyumon (New Introduction to Surface Active Agents)", completely revised version, 1992, page 107.

Examples of the nonionic surface active agent represented by the formula (A) include singly-terminated ester of polyethylene oxide of 2-butyloctanoic acid, polyethylene oxide adduct of undecane-6-ol, etc.

The nonionic surface active agent having a hydrophilic group in the vicinity of the center of hydrophobic moiety is preferably a compound represented by the formula (B).

In the formula (B),  $R^{21}$ ,  $R^{22}$ ,  $R^{23}$  and  $R^{24}$  each independently represents a  $C_1$ - $C_6$ , preferably  $C_1$ - $C_4$  alkyl group, and  $n_1$  and  $n_2$  each represents a number such that the sum of  $n_1$  and  $n_2$  is from 0 to 40, preferably from 2 to 20.

Preferred examples of the nonionic surface active agent represented by the formula (B) include ethylene oxide adducts of acetylene-based diol (SURFYNOL Series (Air Products & Chemicals)), etc., and preferred among these nonionic surface active agents are those having a molecular weight of from 200 to 1,000, more preferably from 300 to 900, particularly from 400 to 900.

By incorporating a surface active agent in the ink for ink jet recording of the present invention to adjust the liquid physical properties such as surface tension of the ink, the ejection stability of the ink can be enhanced, making it possible to exert an excellent effect of improving the water resistance of image and preventing the bleeding of printed ink.

The content of the surface active agent is from 0.001 to 15% by weight, preferably from 0.005 to 10% by weight, more preferably from 0.01 to 5% by weight based on the weight of the ink.

The ink for ink jet recording of the present invention can be prepared by dissolving and/or dispersing the aforementioned azo dye and surface active agent in an aqueous medium. The term "aqueous medium" as used in the present invention is meant to indicate water or a mixture of water and a small amount of a water-miscible organic solvent optionally comprising additives such as wetting agent, stabilizer and preservative incorporated therein.

Examples of the water-miscible organic solvent employable in the present invention include alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, t-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol), polyvalent alcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentanediol, glycerin, hexanetriol, thiodiglycol), glycol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol

monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether, ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylene diamine, diethylene triamine, triethylene tetramine, polyethyleneimine, tetramethylpropylenediamine), and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, 2-pyrrolidone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 2-oxazolidone, 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone). Two or more of the water-miscible organic solvents may be used in combination.

The aforementioned azo dye, if it is oil-soluble, may be emulsion-dispersed in an aqueous medium in the form of solution in a high boiling organic solvent.

The boiling point of the high boiling organic solvent to be used in the present invention is 150°C or more, preferably 170°C or more.

Examples of the high boiling organic solvent include phthalic acid esters (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl)isophthalate, bis(1,1-diethylpropyl)phthalate), phosphoric or phosphonic acid esters (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, dioctyl butyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, di-2-ethylhexyl phenyl phosphate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethylaurylamide), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic esters (e.g., dibutoxyethyl succinate, di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, diethyl azelate, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline, etc.), chlorinated paraffins (e.g., paraffins having a chlorine content of from 10% to 80%), trimesic acid esters (e.g., tributyl trimesate), dodecyl benzene, diisopropylene naphthalene, phenols (e.g., 2,4-di-tert-amylphenol, 4-dodecyloxyphenol, 4-dodecyloxycarbonylphenol, 4-(4-dodecyloxy phenylsulfonyl) phenol), carboxylic acids (e.g., 2-(2,4-di-tert-amylphenoxy)butyric acid, 2-ethoxyoctanedecanoic acid), and alkylphosphoric acids (e.g., di-2(ethylhexyl)phosphoric acid, dipheylphosphoric acid), etc. The high boiling organic

solvent may be used in an amount of from 0.01 to 3 times, preferably from 0.01 to 1.0 times that of the oil-soluble dye by weight.

These high boiling organic solvents may be used singly or in admixture of two or more thereof (e.g., tricresyl phosphate and dibutyl phthalate, trioctyl phosphate and di(2-ethylhexyl)sebacate, dibutyl phthalate and poly(N-t-butylacrylamide)).

Examples of compounds other than the aforementioned high boiling organic solvents to be used in the present invention and/or methods for the synthesis of these high boiling organic solvents are described in US Patents 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321, 5,013,639, European Patents 276,319A, 286,253A, 289,820A, 309,158A, 309,159A, 309,160A, 509,311A, 510,576A, East German Patents 147,009, 157,147, 159,573, 225,240A, British Patent 2,091,124A, JP-A-48-47335, JP-A-50-26530, JP-A-51-25133, JP-A-51-26036, JP-A-51-27921, JP-A-51-27922, JP-A-51-149028, JP-A-52-46816, JP-A-53-1520, JP-A-53-1521, JP-A-53-15127, JP-A-53-146622, JP-A-54-91325, JP-A-54-106228, JP-A-54-118246, JP-A-55-59464, JP-A-56-64333, JP-A-56-81836, JP-A-59-204041, JP-A-61-84641, JP-A-62-118345, JP-A-62-247364, JP-A-63-167357, JP-A-63-214744, JP-A-63-301941, JP-A-64-9452, JP-A-64-9454, JP-A-64-68745, JP-A-1-101543, JP-A-1-102454, JP-A-2-792, JP-A-2-4239, JP-A-2-43541, JP-A-4-29237, JP-A-4-30165, JP-A-4-232946, JP-A-4-346338, etc.

The aforementioned high boiling organic solvents are used in an amount of from 0.01 to 3.0 times, preferably from 0.01 to 1.0 times that of the oil-soluble dye by weight.

In the present invention, the oil-soluble dye and the high boiling organic solvent are used in the form of emulsion dispersion in an aqueous medium. During emulsion dispersion, a low boiling organic solvent may be used in some cases from the standpoint of emulsifiability. As such a low boiling organic solvent there may be used an organic solvent having a boiling point of from about 30°C to 150°C at atmospheric pressure. For example, esters (e.g., ethyl acetate, butyl acetate, ethyl propionate,  $\beta$ -ethoxyethyl acetate, methyl cellosolve acetate), alcohols (e.g., isopropyl alcohol, n-butyl alcohol, secondary butyl alcohol), ketones (e.g., methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone), amides (e.g., dimethylformamide, N-methylpyrrolidone), ethers (e.g., tetrahydrofuran, dioxane), etc. are preferably used, but the present invention is not limited thereto.

The emulsion dispersion is effected to disperse an oil phase having a dye dissolved



in a high boiling organic solvent optionally mixed with a low boiling organic solvent in an aqueous phase mainly composed of water to make minute oil droplets of oil phase. During this procedure, additives such as surface active agent, wetting agent, dye stabilizer, emulsion stabilizer, preservative and antifungal agent described later may be added to either or both of the aqueous phase and the oil phase as necessary.

The emulsification is normally accomplished by adding the oil phase to the aqueous phase, but a so-called phase inversion emulsification method involving the dropwise addition of an aqueous phase to an oil phase is preferably used as well. Also in the case where the azo dye to be used in the present invention is water-soluble and the additives are oil-soluble, the aforementioned emulsification method may be used.

The emulsion dispersion may be effected with various surface active agents.

For the purpose of stabilizing the ink shortly after emulsification, a water-soluble polymer may be added in combination with the aforementioned surface active agents. As such a water-soluble polymer there may be preferably used a polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide, polyacrylic acid, polyacrylamide or copolymer thereof. Further, natural water-soluble polymers such as polysaccharides, casein and gelatin, etc. may be preferably used. For the purpose of stabilizing the dye dispersion, polyvinyls obtained by the polymerization of acrylic acid esters, methacrylic acid esters, vinyl esters, acrylamides, methacrylamides, olefins, styrenes, vinyl ethers or acrylonitriles, polyurethanes, polyesters, polyamides, polyureas, polycarbonates, etc., which are substantially insoluble in an aqueous medium, may be used in combination. These polymers preferably have  $-\text{SO}_3^-$  or  $-\text{COO}^-$ . In the case where these polymers substantially insoluble in an aqueous medium are used in combination, they are preferably used in an amount of 20% by weight or less, preferably 10% by weight or less based on the amount of the high boiling organic solvent.

In the case where emulsion dispersion is effected to disperse the oil-soluble dye or high boiling organic solvent to make an aqueous ink, a particularly important factor is control over the particle size of the aqueous ink. In order to enhance the color purity or density during the formation of an image by ink ejection, it is essential to reduce the average particle size. The volume-average particle diameter of the aqueous ink is preferably 1  $\mu\text{m}$  or less, more preferably from 5 nm to 100 nm.

The measurement of the volume-average particle diameter and the particle size distribution of the dispersed particles can be easily accomplished by any known method such as static light scattering method, dynamic light scattering method, centrifugal sedimentation method and method as disclosed in "Jikken Kagaku Koza (Institute of Experimental

Chemistry)", 4th ed., pp. 417 – 418. For example, measurement can be easily carried out by diluting the ink with distilled water such that the particle concentration in the ink reaches 0.1% to 1% by weight, and then subjecting the solution to measurement using a commercially available volume-average particle diameter measuring instrument (e.g., Microtrack UPA (produced by NIKKISO CO., LTD.)). Further, dynamic light scattering method utilizing laser doppler effect is particularly preferred because it is capable of measuring even small particle size.

The term "volume-average particle diameter" is meant to indicate average particle diameter weighted with particle volume, which is obtained by dividing the sum of the product of the diameter and the volume of individual particles in the aggregate of particles by the total volume of the particles. The details of volume-average particle diameter are described in Souichi Muroi, "Koubunshi Ratekkusu no Kagaku (Chemistry of Polymer Latexes)", Koubunshi Kankokai, page 119.

It was also made obvious that the presence of coarse particles has an extremely great effect on the printing properties. In other words, coarse particles clog the head nozzle, or even if coarse particles don't go so far as to clog the head nozzle, they form blots whereby the ink cannot be ejected or can be deviated when ejected, giving a serious effect on the printing properties. In order to prevent this trouble, it is important to keep the number of particles of 5  $\mu\text{m}$  or more and 1  $\mu\text{m}$  or more in the resulting ink to 10 or less and 1,000 or less, respectively.

The removal of these coarse particles can be accomplished by any known method such as centrifugal separation method and precision filtration method, etc. The separation step may be effected shortly after emulsion dispersion or shortly before the filling of the emulsion dispersion comprising various additives such as wetting agent and surface active agent in the ink cartridge.

As an effective unit for reducing the average particle diameter of particles and eliminating coarse particles there may be used a mechanical emulsifier.

As such an emulsifier there may be used any known device such as simple stirrer, impeller type agitator, in-line agitator, mill type agitator (e.g., colloid mill, etc.) and ultrasonic agitator, and, the use of a high pressure homogenizer is particularly preferred.

The details of the mechanism of high pressure homogenizer are described in US Patent 4,533,254, JP-A-6-47264, etc., and, examples of commercially available high pressure homogenizers include Gaulin homogenizer (produced by A. P. V GAULLN INC.), microfluidizer (produced by MICROFLUIDEX INC.) and altimizer (produced by SUGINO

MACHINE LIMITED) , etc.

In recent years, a high pressure homogenizer having a mechanism for atomizing a material in a ultrahigh pressure jet stream as disclosed in US Patent 5,720,551 is particularly useful in the emulsion dispersion of the invention. An example of the emulsifier using a ultrahigh pressure jet stream is De BEE2000 (produced by BEE INTERNATIONAL LTD.).

The pressure at which emulsion is carried out by a high pressure emulsion disperser is 50 MPa or more, preferably 60 MPa or more, more preferably 180 MPa or more.

For example, the combined use of two or more emulsifiers as in a method involving the emulsification by an agitated emulsifier followed by the passage through a high pressure homogenizer is particularly preferred. Alternatively, a method is preferably used which comprises effecting the emulsifying dispersion of the material using such an emulsifier, adding additives such as wetting agent and surface active agent, and then passing the ink again through the high pressure homogenizer before being filled in the cartridge.

In the case where the dye composition comprises a low boiling organic solvent incorporated therein in addition to the high boiling organic solvent, it is preferred to remove the low boiling solvent from the standpoint of emulsion stability and safety/hygiene. The removal of the low boiling solvent can be accomplished by any known method depending on the kind of the solvent to be removed. In some detail, evaporation method, vacuum evaporation method, ultrafiltration method, etc. may be used. The step of removing the low boiling organic solvent is preferably effected as rapidly as possible shortly after emulsification.

Manufacturing methods of inks for ink jet are disclosed in detail in JP-A-5-148436, JP-A-5-295312, JP-A-7-97541, JP-A-7-82515 and JP-A-7-118584, and these methods can be used in manufacturing the ink of the present invention.

The ink for ink jet recording obtained in the present invention may comprise properly selected additives incorporated therein in a proper amount such as drying inhibitor for preventing the clogging of the ejection nozzle with dried ink, penetration accelerator for helping the ink to penetrate in the paper, ultraviolet absorber, oxidation inhibitor, viscosity adjustor, surface tension adjustor, dispersant, dispersion stabilizer, antifungal agent, rust preventive, pH adjustor, anti-foaming agent and chelating agent, etc.

As the drying inhibitor in the invention there is preferably used a water-soluble organic solvent having a lower vapor pressure than water. Specific examples of the water-soluble organic solvent include polyvalent alcohols such as ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, thiodiglycol, dithiodiglycol,

2-methyl-1,3-propanediol, 1,2,6-hexanetriol, acetylene glycol derivative, glycerin and trimethylolpropane, etc., lower alkylethers of polyvalent alcohol such as ethylene glycol monomethyl(or ethyl) ether, diethylene glycol monomethyl(or ethyl)ether and triethylene glycol monoethyl(or butyl)ether, etc., heterocyclic compounds such as 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone and N-ethylmorpholine, etc., sulfur-containing compounds such as sulfolane, dimethylsulfoxide and 3-sulfolene, etc., polyfunctional compounds such as diacetone alcohol and diethanolamine, etc., and urea derivatives. Preferred among these water-soluble organic solvents are polyvalent alcohols such as glycerin and diethylene glycol, etc. These drying inhibitors may be used singly or in combination of two or more thereof. These drying inhibitors are preferably incorporated in the ink in an amount of from 10% to 50% by weight.

Examples of the penetration accelerator employable herein include alcohols such as ethanol, isopropanol, butanol, di(tri)ethylene glycol monobutyl ether and 1,2-hexanediol, sodium laurylsulfate, sodium oleate, and nonionic surface active agents, etc. These penetration accelerators can exert a sufficient effect when incorporated in the ink in an amount of from 10% to 30% by weight. These penetration accelerators are preferably used in an amount such that no print bleeding or print through occurs.

Examples of the ultraviolet absorber to be used to enhance the preservability of the image in the present invention include benzotriazole-based compounds as disclosed in JP-A-58-185677, JP-A-61-190537, JP-A-2-782, JP-A-5-197075 and JP-A-9-34057, benzophenone-based compounds as disclosed in JP-A-46-2784, JP-A-5-194483 and US Patent 3,214,463, cinnamic acid-based compounds as disclosed in JP-B-48-30492, JP-A-56-21141 and JP-A-10-88106, triazine-based compounds as disclosed in JP-A-4-298503, JP-A-8-53427, JP-A-8-239368, JP-A-10-182621 and JP-T-8-501291, compounds as disclosed in Research Disclosure No. 24239, and compounds which absorb ultraviolet rays to emit fluorescence, i.e., so-called fluorescent brighteners, such as stilbene-based and benzoxazole-based compounds.

In the present invention, as the oxidation inhibitor to be used to enhance the image preservability there may be used any of various organic and metal complex-based fading inhibitors. Examples of the organic fading inhibitors include hydroquinones, alkoxyphenols, dialkoxyphenols, phenols, anilines, amines, indanes, chromans, alkoxyanilines, and heterocyclic compounds, and, examples of the metal complex-based fading inhibitors include nickel complex, and zinc complex. Specific examples of these oxidation inhibitors include compounds listed in the patents cited in Research Disclosure No. 176P43, Articles VI-I and J,

Research Disclosure No. 15162, Research Disclosure No. 18716, left column, page 650, Research Disclosure No. 36544, page 527, Research Disclosure No. 307105, page 872, and Research Disclosure No. 15162, and compounds included in the formula and examples of representative compounds listed in JP-A-62-215272, pp. 127 – 137.

Examples of the antifungal agent to be used in the present invention include sodium dehydroacetate, sodium benzoate, sodium pyridinethione-1-oxide, ethyl p-hydroxybenzoate, 1,2-benzisothiazoline-3-one, and salts thereof. These antifungal agents are preferably incorporated in the ink in an amount of from 0.02% to 5.00% by weight.

The details of these antifungal agents are described in “Bokin Bobizai Jiten (Dictionary of Anti-bacterial and Antifungal Agents)”, compiled by Dictionary Compilation Committee of The Society for Antibacterial and Antifungal Agents, Japan.

Examples of the rust preventive include acidic sulfites, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite, and benzotriazole. These rust preventives are preferably incorporated in the ink in an amount of from 0.02% to 5.00% by weight.

The pH adjustor to be used in the present invention is preferably used for the purpose of adjusting the pH value, providing dispersion stability or like purposes. It is preferred that the pH value of the ink be adjusted to a range of from 8 to 11 at 25°C. When the pH value of the ink falls below 8, the resulting dye exhibits a deteriorated solubility, causing nozzle clogging, and, on the contrary, when the pH value of the ink exceeds 11, the resulting ink tends to exhibit a deteriorated water resistance. Examples of the pH adjustor include basic pH adjustors such as organic base and inorganic alkali, and acidic pH adjustors such as organic acid and inorganic acid.

Examples of the aforementioned organic base include triethanolamine, diethanolamine, N-methyldiethanolamine, dimethylethanolamine, etc. Examples of the aforementioned inorganic alkali include hydroxide of alkaline metal (e.g., sodium hydroxide, lithium hydroxide, potassium hydroxide), carbonate of alkaline metal (e.g., sodium carbonate, sodium hydrogen carbonate), and ammonium. Further, examples of the aforementioned organic acid include acetic acid, propionic acid, trifluoroacetic acid, alkylsulfonyl acid, etc. Examples of the aforementioned inorganic acid include hydrochloric acid, sulfuric acid, phosphoric acid, etc.

The viscosity of the ink of the present invention is preferably 30 mPa·s or less, more preferably 20 mPa·s or less. For adjustment of viscosity, a viscosity adjustor may be used. Examples of the viscosity adjustor include celluloses, water-soluble polymers such as

polyvinyl alcohol, and nonionic surface active agents. The details of these viscosity adjustors are described in “Nendo Chousei Gijutsu (Technology for Viscosity Adjustment)”, Gijutsu Joho Kyoukai, Article 9, 1999, and “Inku Jetto Purintayou Kemikaruzu (98 zouho) – Zairyou no Kaihatsu Doko/Tenbo Chousa (Chemicals for Ink Jet Printer (98 enlarged edition) – Research on Trend and View of Development of Materials)”, CMC, pp. 162 – 174, 1997.

In the present invention, surface active agents including the aforementioned nonionic, cationic or anionic surface active agents may be used as a dispersant or a dispersion stabilizer, and chelating agents including fluorine-containing compound, silicone compound or EDTA may be used as a defoaming agent.

The recording paper and recording film on which an image is drawn with the ink of the present invention will be described hereinafter. In the present invention, known recording materials, i.e., ordinary paper, resin-coated paper, paper dedicated to ink jet recording as described in JP-A-8-169172, JP-A-8-27693, JP-A-2-276670, JP-A-7-276789, JP-A-9-323475, JP-A-62-238783, JP-A-10-153989, JP-A-10-217473, JP-A-10-235995, JP-A-10-337947, JP-A-10-217597, JP-A-10-337947, etc., paper dedicated also to electrophotography, cloth, film, glass, metal, pottery, etc. may be used.

The recording paper and recording film for use in ink jet printing with the ink of the present invention will be described hereinafter. As the support in the recording paper and recording film there may be used one obtained by processing a chemical pulp such as LBKP and NBKP, a mechanical pulp such as GP, PGW, RMP, TMP, CTMP, CMP and CGP, used paper pulp such as DIP or the like, optionally mixed with known additives such as pigment, binder, sizing agent, fixing agent, cationic agent and paper strength improver, through various paper machines such as foundrinier paper machine and cylinder paper machine. As the support there may be used either a synthetic paper or plastic film sheet besides these support, and the thickness of the support is preferably from 10  $\mu\text{m}$  to 250  $\mu\text{m}$  and the basis weight of the support is preferably from 10 to 250  $\text{g/m}^2$ .

An image-receiving layer and a back coat layer may be provided on the support directly or with a size press or anchor coat layer of starch, polyvinyl alcohol or the like interposed therebetween to prepare a material for a receiving material of the ink of the present invention. The support may be further subjected to leveling using a calendering machine such as machine calender, TG calender and soft calender.

In the present invention, as the support there is preferably used a paper or plastic film laminated with a polyolefin (e.g., polyethylene, polystyrene, polybutene, copolymer thereof) or polyethylene terephthalate on both sides thereof. The polyolefin preferably

comprises a white pigment (e.g., titanium oxide, zinc oxide) or a tinting dye (e.g., cobalt blue, ultramarine, neodymium oxide) incorporated therein.

The image-receiving layer to be provided on the support will be described hereinafter. The image-receiving layer comprises a porous material or aqueous binder incorporated therein. The image-receiving layer also preferably comprises a pigment incorporated therein, and as such a pigment there is preferably used a white pigment. Examples of the white pigment employable herein include inorganic white pigments such as calcium carbonate, kaolin, talc, clay, diatomaceous earth, synthetic amorphous silica, aluminum silicate, magnesium silicate, calcium silicate, aluminum hydroxide, alumina, lithopone, zeolite, barium sulfate, calcium sulfate, titanium dioxide, zinc sulfate and zinc carbonate, and organic pigments such as styrene-based pigment, acrylic pigment, urea resin and melamine resin. Particularly preferred among these pigments are porous inorganic white pigments, and in particular, synthetic amorphous silica having a large pore area, etc. are preferred. As the synthetic amorphous silica there may be also used anhydrous silicate obtained by dry method (gas phase method) or hydrous silicate obtained by wet method.

Specific examples of the recording paper comprising the aforementioned pigments incorporated in the image-receiving layer include those disclosed in JP-A-10-81064, JP-A-10-119423, JP-A-10-157277, JP-A-10-217601, JP-A-11-348409, JP-A-2001-138621, JP-A-2000-43401, JP-A-2000-211235, JP-A-2000-309157, JP-A-2001-96897, JP-A-2001-138627, JP-A-11-91242, JP-A-8-2087, JP-A-8-2090, JP-A-8-2091, JP-A-8-2093, JP-A-174992, JP-A-11-192777, JP-A-2001-301314, etc.

Examples of the aqueous binder to be incorporated in the image-receiving layer include water-soluble polymers such as polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationated starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinyl pyrrolidone, polyalkylene oxide and polyalkylene oxide derivative, water-dispersible polymers such as styrene butadiene latex and acryl emulsion, etc. These aqueous binders may be used singly or in combination of two or more thereof. In the present invention, particularly preferred among these aqueous binders are polyvinyl alcohol and silanol-modified polyvinyl alcohol from the standpoint of adhesion to pigment and exfoliation resistance of ink-receiving layer.

The image-receiving layer may comprise a mordant, a waterproofing agent, a light-resistance improver, a gas resistance improver, a surface active agent, a film hardener and other additives incorporated therein besides the pigments and aqueous binders.

The mordant to be incorporated in the image-receiving layer is preferably passivated.

To this end, a polymer mordant is preferably used in terms of bleeding resistance.

For the details of the polymer mordant, reference can be made to JP-A-48-28325, JP-A-54-74430, JP-A-54-124726, JP-A-55-22766, JP-A-55-142339, JP-A-60-23850, JP-A-60-23851, JP-A-60-23852, JP-A-60-23853, JP-A-60-57836, JP-A-60-60643, JP-A-60-118834, JP-A-60-122940, JP-A-60-122941, JP-A-60-122942, JP-A-60-235134, JP-A-1-161236, US Patents 2,484,430, 2,548,564, 3,148,061, 3,309,690, 4,115,124, 4,124,386, 4,193,800, 4,273,853, 4,282,305 and 4,450,224. An image-receiving material containing a polymer mordant disclosed in JP-A-1-161236, pp. 212 to 215 is particularly preferable. The use of the polymer mordant disclosed in the above cited patent makes it possible to obtain an image having an excellent quality free of bleeding and hence improve the light-resistance of the image.

The waterproofing agent can be used to render the image waterproof, and as such a waterproofing agent there is preferably used a cationic resin in particular. Examples of such a cationic resin include polyamide polyamine epichlorohydrin, polyethylenimine, polyamine sulfone, dimethyl diallyl ammonium chloride polymer, and cation polyacrylamide. The content of such a cationic resin is preferably from 1% to 15% by weight, particularly from 3% to 10% by weight based on the total solid content of the ink-receiving layer.

Examples of the light-resistance improver and gas resistance improver include phenol compounds, hindered phenol compounds, thioether compounds, thiourea compounds, thiocyanic acid compounds, amine compounds, hindered amine compounds, TEMPO compounds, hydrazine compounds, hydrazide compounds, amidine compounds, vinyl-containing compounds, ester compounds, amide compounds, ether compounds, alcohol compounds, sulfinic acid compounds, saccharides, water-soluble reducing compounds, organic acids, inorganic acids, hydroxyl-containing organic acids, benzotriazole compounds, benzophenone compounds, triazine compounds, heterocyclic compounds, water-soluble metal salts, organic metal compounds, and metal complexes.

Specific examples of these compounds include those disclosed in JP-A-10-182621, JP-A-2001-260519, JP-A-2000-260519, JP-B-4-34953, JP-B-4-34513, JP-B-4-34512, JP-A-11-170686, JP-A-60-67190, JP-A-7-276808, JP-A-2000-94829, JP-T-8-512258, and JP-A-11-321090.

The surface active agent acts as a coating aid, releasability improver, slipperiness improver or antistat. For the details of the surface active agent, reference can be made to JP-A-62-173463 and JP-A-62-183457.

An organic fluoro-compounds may be used instead of the surface active agent. The



organic fluoro-compound is preferably hydrophobic. Examples of the organic fluoro-compound include fluorine-based surface active agents, oil-based fluorine compounds (e.g., fluorine-based oil), and solid fluorine-based compound resins (e.g., tetrafluoroethylene resin). For the details of the organic fluoro-compound, reference can be made to JP-B-57-9053 (8th to 17th columns), JP-A-61-20994, and JP-A-62-135826.

As the film hardener there may be used any of materials disclosed in JP-A-1-161236, page 222, JP-A-9-263036, JP-A-10-119423, and JP-A-2001-310547.

Other examples of additives to be incorporated in the image-receiving layer include pigment dispersants, thickening agents, antifoaming agents, dyes, fluorescent brighteners, preservatives, pH adjustors, matting agents, and film hardeners. There may be provided one or two ink-receiving layers.

The recording paper and recording film may comprise a back coat layer provided thereon. Examples of the components which can be incorporated in the back coat layer include white pigments, aqueous binders, and other components.

Examples of the white pigments to be incorporated in the back coat layer include inorganic white pigments such as light calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminum hydroxide, alumina, lithopone, zeolite, hydrated halloysite, magnesium carbonate and magnesium hydroxide, and organic pigments such as styrene-based plastic pigment, acrylic plastic pigment, polyethylene, microcapsule, urea resin and melamine resin.

Examples of the aqueous binder to be incorporated in the back coat layer include water-soluble polymers such as styrene/maleate copolymer, styrene/acrylate copolymer, polyvinyl alcohol and silanol, and water-dispersible polymers such as styrenebutadiene latex and acryl emulsion. Examples of other components to be incorporated in the back coat layer include antifoaming agents, foaming inhibitors, dyes, fluorescent brightening agents, preservatives, and waterproofing agents.

The layers (including back layer) constituting the ink jet recording paper and film may comprise a dispersion of polymer fine particles incorporated therein. The dispersion of polymer fine particles is used for the purpose of improving physical properties of film, e.g., stabilizing dimension, inhibiting curling, adhesion and film cracking. For the details of the dispersion of polymer fine particles, reference can be made to JP-A-62-245258, JP-A-62-1316648, and JP-A-62-110066. The incorporation of a dispersion of polymer fine

particles having a low glass transition temperature (40°C or less) in a layer containing a mordant makes it possible to prevent the cracking or curling of the layer. The incorporation of a dispersion of polymer fine particles having a high glass transition temperature, too, in the back layer makes it possible to prevent the curling of the back layer.

The ink jet recording method to which the ink of the invention is applied is not limited, and the ink of the present invention may be used in any known recording method such as electrostatic control method which utilizes electrostatic attraction to eject ink, drop-on-demand method (pressure pulse method) utilizing vibrational pressure of piezoelectric element, acoustic ink jet method which comprises converting electrical signal to acoustic beam with which the ink is irradiated to produce a radiation pressure that is utilized to eject the ink and thermal ink jet (bubble jet) method which comprises heating the ink to form bubbles that raise the pressure.

Examples of the ink jet recording method include a method which comprises ejecting many portions of an ink having a low concentration called photoink in a small volume, a method which comprises using a plurality of inks having substantially the same hue but different densities to improve the image quality, and a method involving the use of a colorless transparent ink.

#### [Examples]

The present invention will be further described in the following examples, but the present invention is not construed as being limited thereto.

#### (Example 1)

To the following components was added deionized water to make 1 l, and the mixture was then heated to 30°C to 40°C with stirring for 1 hour. Thereafter, the solution was filtered through a microfilter having an average pore diameter of 0.25 µm under reduced pressure to prepare a light magenta ink.

Magenta dye (a-36)	10.2 g/L
Triethylene glycol monobutyl ether	130 g/L
Glycerin	130 g/L
Diethylene glycol	150 g/L
Triethanolamine	7.0 g/L
Benzotriazole	0.07 g/L
PROXEL XL2 (Zeneca Inc.)	5.0 g/L
Surface active agent	6.0 g/L

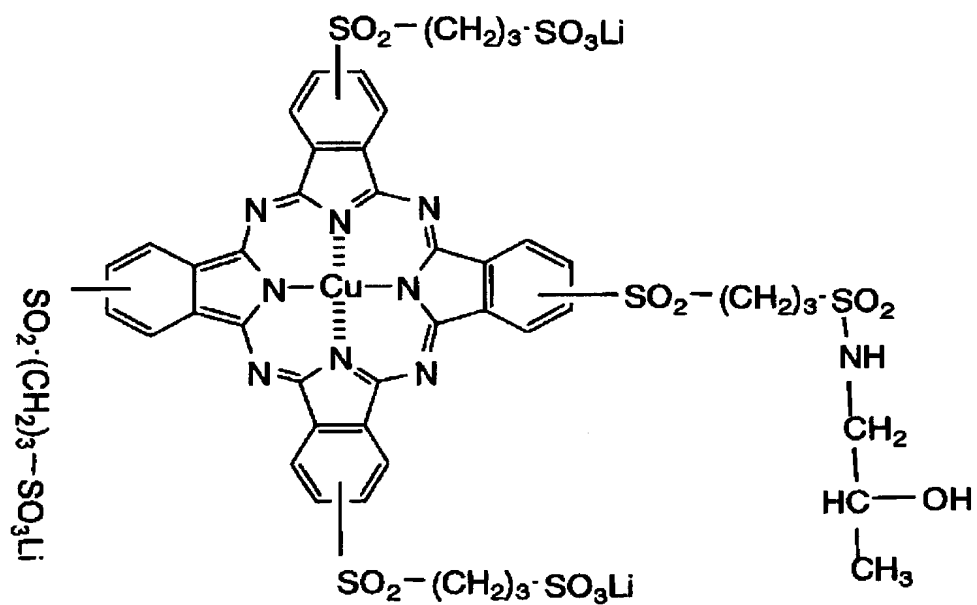
(Singly terminated 2-butyloctanoic acid ester of polyethylene glycol (average

number of repetition of ethylene oxide: 10)

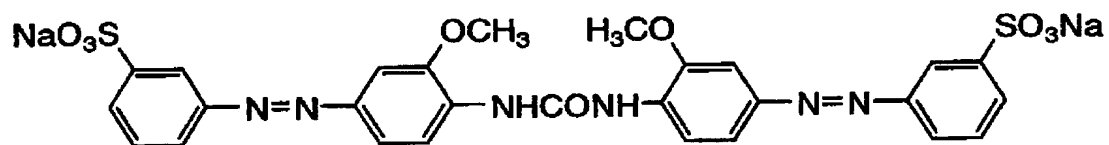
Further, the kind of dyes and the additives were changed to prepare a magenta ink, a light cyan ink, a cyan ink, a yellow ink and a black ink from which an ink set 101 set forth in Table below was then prepared.

	Light magenta	Magenta	Light cyan	Cyan	yellow	Dark yellow	Black
Dye	(a-36) 10.2 g/l	(a-36) 30.8	A-2 17.5	A-2 68	A-3 14.7 A-4 14.0	A-3 10.3 A-4 9.8 A-2 13.6	A-5 20.0 A-6 39.0 A-7 17.0 A-3 20.0 -
Triethylene glycol monobutyl ether	130	140	119	127	130	130	-
Diethylene glycol monobutyl ether	-	-	-	-	-	-	230
Glycerin							
Diethylene glycol	130	160	123	110	150	138	120
Triethanolamine	150	110	164	107	160	144	20
Urea	7	7	6.5	10	1	4	18
2-Pyrrolidone	37	46	-	-	-	-	-
Proxel XLII (g/l)	40	-	-	20	-	-	80
	5.0	4.5	1.0	4.0	3.0	3.0	4.0
Benzotriazole							
Surface active agent	0.07 6	0.08 12	0.07 10	0.09 10	0.06 3	0.07 5	0.08 5

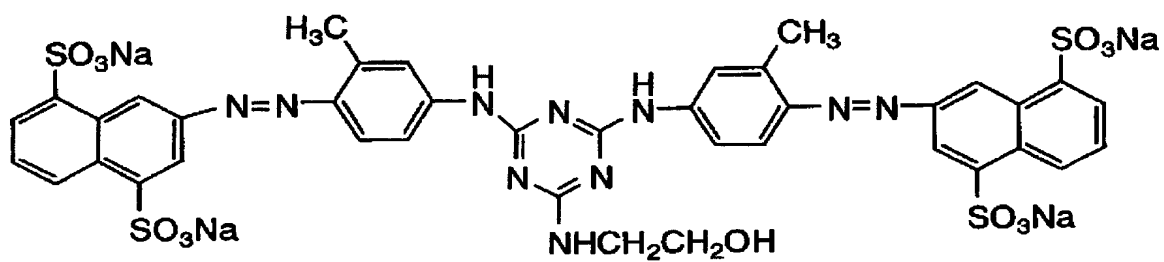
A-2



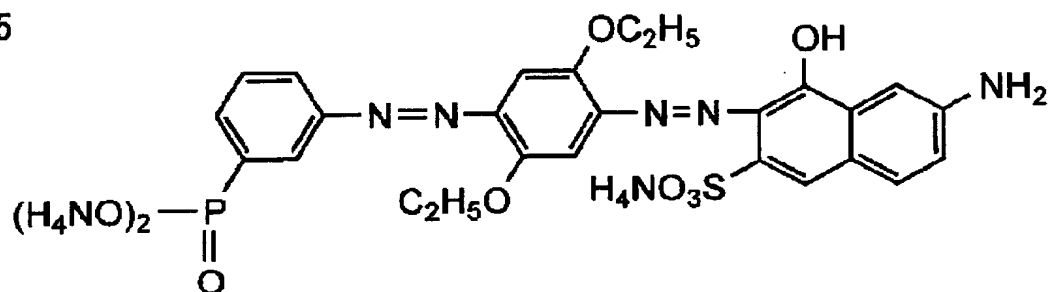
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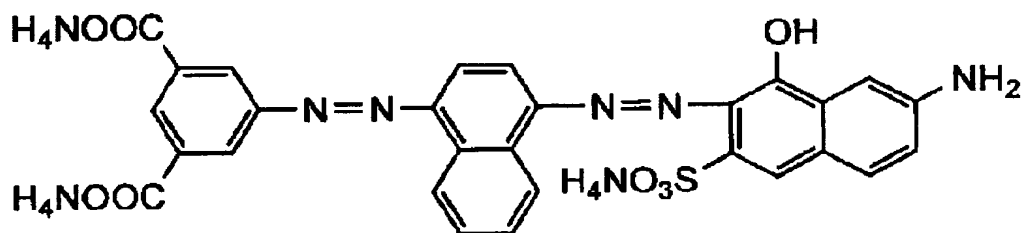
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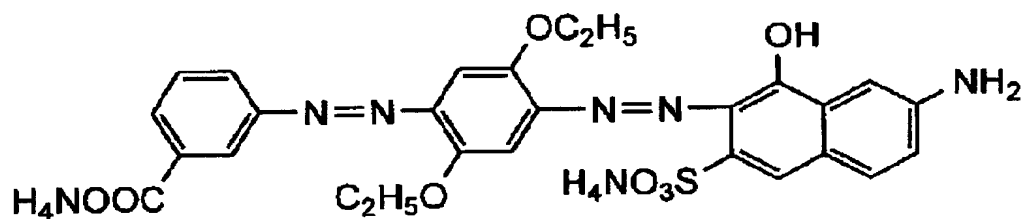
A-5



A-6



A-7



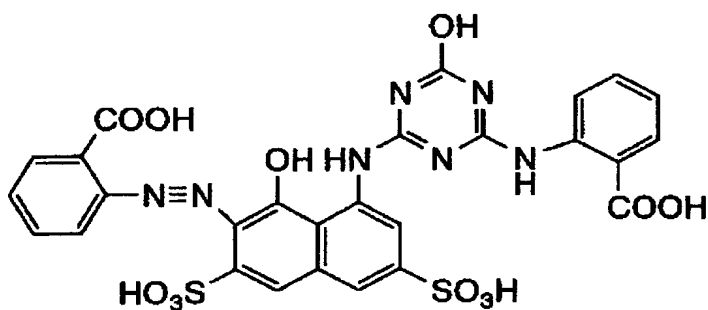
Subsequently, ink sets 102 to 107 were prepared in the same manner as the ink set 101 except that the amount of surface active agent and the kind and amount of organic solvent of the invention in light cyan ink and cyan ink were changed according to Tables below. The static surface tension of these inks were measured using a Type CBVP-A3 automatic surface tension meter (Kyowa Interface Science Co., Ltd.). Further, the dynamic surface tension of these inks were measured using a Type BP-D3 automatic dynamic surface tension meter (Kyowa Interface Science Co., Ltd.).

Ink set		Light magenta	Magenta	Static surface tension light magenta /m	Dynamic surface tension light magenta /m	Static surface tension light magenta /m	Dynamic surface tension light magenta /m	Remarks
301	Dye Surface agent	a-36 6	a-36 12	33.5 mN/m	34.9 mN/m	33.9 mN/m	34.7 mN/m	Inventive
	Diethylene glycol Glycerin	150	110					
	Triethylene glycol	130	160					
	monobutyl ether	130	140					
302	Dye Surface agent	a-3 10	a-36 10	33.9	35.9	33.7	34.6	Inventive
	Diethylene glycol Glycerin	30	35					
	Triethylene glycol	5	8					
	monobutyl ether	50	47					
303	Dye Surface agent	a-36 10	a-36 10	34.1	36.2	33.3	33.8	Inventive
	Diethylene glycol Glycerin	30	35					
	Triethylene glycol	5	8					
	monobutyl ether	-	-					
304	Dye Surface agent	a-36 10	a-36 10	37.8	38.9	38.9	38.9	Inventive
	Diethylene glycol Glycerin	150	110					
	Triethylene glycol	130	130					
	monobutyl ether	130	140					

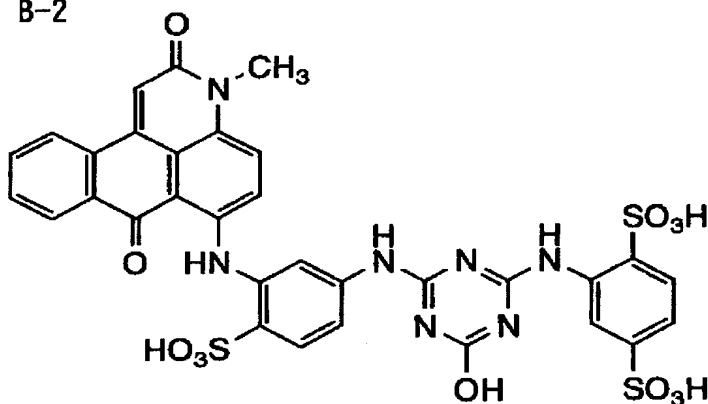
305	Dye Surface agent	active	a-36 -	a-36 -	52.7	51.9	53.6	52.7	Reference
	Diethylene glycol Glycerin		30	35					
	Triethylene glycol monobutyl ether		5	8					
306	Dye Surface agent	active	a-36 10	a-36 10	24.2	24.6	23.7	23.7	Reference
	Diethylene glycol Glycerin		150	110					
	Triethylene glycol monobutyl ether		130 130	130 140					
307	Dye Surface agent	active	B-1 6	B-2 12	32.3	3 3 . 7	3 2 . 3	33.1	Comparative
	Diethylene glycol Glycerin		150	110					
	Triethylene glycol monobutyl ether		130 130	160 140					



B-1



B-2



(Ink jet recording)

Subsequently, the ink sets 101 to 107 were each packed in the cartridge of a Type PM920C ink jet printer (produced by SEIKO EPSON CO., LTD.) by which an image was then printed on an ink jet paper photographic gloss paper EX produced by Fuji Photo Film Co., Ltd. and evaluated for the following properties.

For the evaluation of ejection stability ( i ), the cartridge was set in the printer in which the ejection of the ink through all the nozzles was then confirmed and printing was made on 20 sheets of A4 size paper to evaluate disturbance in print.

A: No disturbance in print between the beginning and the termination of printing;

B: Output generated with disturbance in print;

C: Disturbance in print between the beginning and the termination of printing

For the evaluation of ejection stability ( ii ), the cartridge was allowed to stand at 60°C for 2 days, and then evaluated for disturbance in print in the same manner as in ejection

stability ( i ).

For the evaluation of dryability, stain attached to finger when brought into contact with the image shortly after printing was visually evaluated.

○: Acceptable level, Δ: Slightly poor level, x: Unacceptable level

For the evaluation of fine line bleeding ( i ), a fine line pattern of yellow, magenta, cyan and black was printed and visually observed.

○: Acceptable level, Δ: Slightly poor level, x: Unacceptable level

For the evaluation of fine line bleeding ( ii ), for black, a magenta ink was solid-printed, a fine line of black was printed thereon, and bleeding by the contact of the two colors was then evaluated.

○: Acceptable level, Δ: Slightly poor level, x: Unacceptable level

For the evaluation of water resistance, the image obtained was dipped in deionized water for 10 seconds, and then evaluated for bleeding.

○: Acceptable level, Δ: Slightly poor level, x: Unacceptable level

For the evaluation of fine line bleeding ( i ), a fine line pattern of yellow, magenta, cyan and black was printed and visually observed.

○: Acceptable level, Δ: Slightly poor level, x: Unacceptable level

For the evaluation of water resistance, the image obtained was dipped in deionized water for 10 seconds, and then evaluated for bleeding.

○: Acceptable level, Δ: Slightly poor level, x: Unacceptable level

The results thus obtained are set forth in Tables below.

Ink set	Ejection stability (ii)	Ejection stability (ii)	Dryability	Fine bleeding (i)	Fine bleeding (i)	Water resistance
301	A	A	o	o	o	o
302	A	A	o	o	o	o
303	A	A	o	o	o	o
304	A	A	o	Δ	Δ	o
305	B	C	o	X	X	o
306	C	C	o	X	X	o
307	A	A	o	o	o	o

Ink set	Light fastness	Heat fastness	Ozone fastness	Remarks
301	A	A	A	Inventive
302	A	A	A	Inventive
303	A	A	A	Inventive
304	A	A	A	Inventive
305	A	A	A	Comparative
306	A	A	A	Comparative
307	C	A	C	Comparative

It is apparent that when the ink of the present invention is used, an excellent ejection stability can be obtained and excellent properties of water resistance and fastness can be exhibited as well. Further, the ink of the present invention exhibits excellent properties without bleeding during the output of fine line.

Moreover, the inks of the present invention (101 to 104) provided the same hue as provided by the ink (107) comprising the dyes B-1 and B-2, which had been found to have an excellent hue.

Further, the inks of the present invention prepared in the same manner as in Example 1 except that other water-soluble dyes represented by the formula (1) were used instead of the magenta dye (a-36) had the same effect on weathering resistance, ejection stability and hue as that of Example 1.

Further, even when the image-receiving paper to be used in the present invention is changed to PM photographic paper produced by EPSON CO., LTD. or PR101 produced by Canon Inc., the same effects as mentioned above can be exerted.

#### [Advantage of the Invention]

In accordance with the present invention, an ink for ink jet recording can be provided, which has a high ejection stability and an excellent weathering resistance, causes no defects in water resistance and line bleeding and which is an aqueous ink giving practical properties in handleability, odor, safety, etc. as well.

[Designation of Document] ABSTRACT

[Abstract]

[Problem to be solved]

To provide an ink for ink jet recording which exhibits a high stability in ejection, is provided with a hue, is excellent in weathering resistance and causes no defects in water resistance and image quality.

[Means to solve the problem]

An ink for ink jet recording includes at least one dye having a specific structure, dissolved or dispersed in the aqueous medium, in which the ink has a static surface tension of from 25 to 50 mN/m at 25°C.

[Selected drawing] None